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A Review of the Preparation, Characterization and Surface Active Nature of Inorganic and Organic Xerogels and Aerogels

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**A Review of the Preparation, Characterization and
Surface Active Nature of Inorganic and Organic
Xerogels and Aerogels.**

Prepared for DRES

by

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Introduction

For over fifty years, coal-based activated porous carbons have been used as the adsorbent material and catalyst support in military gas masks used by the Canadian Forces and many other armed forces around the world. Impregnation of the carbon by inorganic catalysts and more recently with amines provides protection of the gas mask user against a variety of toxic gases and vapours deemed to be likely chemical agents. The need for such protective devices had not disappeared with the end of the so-called cold war. On the contrary, the increasing threat of terrorist attacks using toxic agents has increased the need for military and other personnel to be able to protect themselves against a wider range of substances than before. There is a need to respond to this increased threat by developing masks that afford protection against a range of toxic industrial materials as well as military agents. At the same time, the possibility of reducing the size and modifying the geometry of the traditional canister, to increase the comfort level and thereby the operational efficiency of the user, are desirable goals for the next generation of gas masks.

Incremental improvements in the performance of impregnated particulate carbons have been made over the years, and further improvements could well be made in the future as techniques are developed to modify the pore structure of the carbon in a more controlled manner. Similarly, one can also try to find more efficient catalysts to render toxic gases and vapours less harmful, and to act against a wider variety of substances. However, a possibly more productive strategy is to explore the potential of novel porous materials, both carbonaceous and non-carbonaceous.

This report describes in some detail the chemistry of aerogel and xerogel formation, and gives examples of the types of materials that could replace particulate carbon in the development of more efficient, shaped monolithic adsorbents and catalyst supports for use in gas masks. An earlier review submitted to DRES in September 1998 focused on activated carbon fibres as possible alternatives to particulate carbons. Such materials are already receiving attention from several research groups in the US and UK, however it is felt by the Active Carbon Group at RMC that, although some improvements might be achieved using carbon fibre based canisters, monolithic porous xerogels could well allow the development of lighter, more comfortable and ergonomically more acceptable gas masks for the CF. Members of the Active Carbon Group at RMC have been involved in research into the synthesis of non-carbonaceous and carbonaceous xerogels for gas storage and separation purposes. The facility to incorporate other functional groups, including amines, into the xerogel or aerogel network, including the surface, in a stable manner is one example of the advantages that these materials can offer. The experience gained in this area puts the group in a strong position to become a leading player in the development of innovative systems for use in both individual and group protection against chemical agents.

1. Overview

This report is written in the style of a review and took into consideration the comments of Mike Evans, David Quinn and Jayne MacDonald as to some of the points of interest with regards to the commissioning agent, DRES.

I have therefore given a general description of the sol-gel process and the two major branches that it comprises: 1. Particulate sol-gel processing and 2. Alkoxide derived sol-gel processing. In some respects the former is confined to the area of metal oxide precursors, such as sodium silicate, silicic acid, nickel oxide etc., and the latter to organometallic precursors, most particularly the organometallic alkoxides such as tetraethylorthosilicate, also known as tetraethoxysilane. Silica dominates both branches, though a considerable amount of work has focused on other non-silica precursors, multicomponent oxides and carbon precursors, the so called organic xero- and aerogels.

Sol-gel processing may be viewed as the preparation of a sol from one of the above precursor branches, which subsequently gels and dries by 'evaporation' of the solvent, to ultimately form a xerogel or aerogel. Gels such as these have been defined as a "dispersed sol transformed into a continuous capillary framework interpenetrated by the original liquid." All of these terms will be defined in the main text. Following the initial dispersion of the precursors both the particulate and alkoxide sol-gel processes share considerable similarities in their growth mechanisms and to a lesser extent in their structural evolution. This commonality is reflected in the text of the report, where for instance, the section on adsorption is concerned with the adsorption behaviour primarily of silica, irrespective of its origin.

The sol-gel technique embraces a wide range of chemistry (table 1 [111]). This report presents a limited but varied overview of the discipline focusing on areas considered of interest to DRES. Other areas of interest to be found are adsorption, catalysts, filters and catalytic detoxification.

The sol-gel process for both the inorganic and organic precursors, is described in some detail in order that the reader understand the flexibility of the materials arising out of the technique.

Some potentially interesting approaches utilizing the technique are mentioned at the end of the report in the Catalytic detoxification section. An appendix giving some details of the several literature searches conducted and the databases accessed is included.

2. The sol-gel process

Materials that are used to coat and insulate the Space Shuttle, the Pathfinder Rover and additionally to capture cosmic dust, are some of the more exotic examples of the lightest, most insulating, and lowest refractive index material next to air [1]. These are some of the extraordinarily unique properties of silica aerogels (figure 1 [2]). Indeed it was the low refractive index which led to their use as Cerenkov detectors, in place of compressed air, which naturally evolved into their use in space [3].

Aerogels are not restricted to silica and generally speaking can be produced from essentially any metal oxide, metal nitrate etc. Silica dominates the field however and will be referred to most often to illustrate the technology.

3. Particulate / Colloidal silica

1. Hydrosols and hydrogels

Silica can be produced in several gel forms, such as colloidal, leading to xerogel and aerogel, or pyrogenic, precipitated or non-aggregated silica [4]. In the colloidal case a metal oxide suspension or sol is formed by mixing colloidal particles in water at a pH greater than 7. *Colloids* are nanosized entities dispersed in a fluid and a *sol* is a dispersion of colloid particles, that are inhibited from precipitation. For silica these sols are manufactured by passing a dilute solution of sodium silicate through a hydrogen exchange resin to produce silicic acid. When a solution of this monomer reaches a concentration of 100-200ppm it 'polymerizes' by condensation of the silanol groups. Polymerization here consists of the association or condensation of silicate species into dimers and trimers by an ionic mechanism and to higher discrete particles which then aggregate into chains (figure 2 [5]). The rate of this process depends on the $[\text{OH}^-]$ and $[\text{H}^+]$. Cyclic polymers add monomers and link to other cyclic polymers to form a three dimensional network, condensing internally to the most compact state, SiOH (silanol groups) facing outwards [5]. The spherical units are the nuclei that develop into larger particles (figure 3 [5]). These growing silica polymers are termed *hydrosols*. Particle size can be varied by adjusting temperature and pH. At a pH of above 7, in the absence of salts, or below 7 in the presence of a low concentration of salts, aggregation of the particles begins to occur leading to gelation and the formation of a *hydrogel*, evident from the time when the hydrosol ceases to flow like a liquid. The pores of the hydrogel, as the term suggests are filled with the liquid in which the gel was prepared which permeates throughout the entire network. A *gel* can be thought of as a viscoelastic body that has interconnected pores in the submicron range. Between pH 7 - 10.5, the negatively charged particles repel each other and growth continues without aggregation. Particle growth and aggregation as such are therefore distinct processes that may overlap. Silica gel may also be defined as a three

dimensional network of aggregated silica particles of colloidal dimensions ($<1000\text{nm}$).

2. Xerogels

A typical manufacturing process of silica gel is shown in figure 4 [6]. This process illustrates some important features. By maintaining a low pH the final product is of high surface area ($>700\text{m}^2/\text{g}$) and consists of small primary particles ($1\text{-}3\text{nm}$). At higher pH the primary particles grow to a larger size of lower surface area ($\sim 400\text{m}^2/\text{g}$). Drying of the low pH hydrogel at atmospheric pressure causes considerable shrinkage due to the enormous capillary pressures (up to 2000atm) leading to *xerogels* of high density, termed regular density xerogels ($1 - 1.5\text{g/mL}$). Drying of the higher pH hydrogel produces xerogel of lower density, by virtue of the larger particle size and lower associated capillary pressure, termed intermediate density xerogels ($0.7 - 1.2\text{g/mL}$).

3. Aerogels

Shrinkage, and hence density of the gel, can be reduced still further by exchanging the gel fluid, water, for alcohol (termed an *alcogel*) or a number of other lower surface tension liquids. If this approach is taken to its limit then supercritical drying of the alcogel, reduces the capillary pressure to zero, and results in an *aerogel* [7]. This procedure will be discussed in more detail in the aerogel section. pH also has a controlling effect on the shrinkage and hence density. At $\text{pH}=4$ hydrogels composed of smaller particles, due to the lower rates of polymerization and depolymerization (figure 5 [5]), undergo the greatest shrinkage. At higher pH, >6 , the growth of larger particles reduces shrinkage, due to a combination of processes such as the higher solubility of silica, the higher rates of dissolution (siloxane bond hydrolysis - Si-O-Si) and deposition of the smaller, more soluble silica particles onto larger ones which coarsens the structure so that it better resists shrinkage. Larger pores are also formed as a result of these processes at higher pH, which reduces the capillary pressure.

Particulate networks consist therefore of identifiable dense primary particles with sizes greater than 1nm that may or may not aggregate in solution, depending on a variety of factors which may be collectively grouped as anything which destabilizes the particle charge and causes aggregation and gelation. Stabilization of the charge prevents agglomeration and the particles remain suspended as a sol. Polymeric systems do not have dense particles $>1\text{nm}$. Since this size marks the lower bound of the colloidal range then they do not contain dense colloids. Admittedly these distinctions are not absolutely definitive, since polymerization is a feature of particulate growth and these particles can be very small $<5\text{nm}$, or approaching the size range of a polymeric species [8].

4. Polymeric silica from silicon alkoxides

1. Precursor

Xerogels and aerogels can be formed from liquid alkoxide precursors, typified by $\text{Si}(\text{OR})_4$, rather than colloidal powders. R can be any organic substituent providing it can form an alkoxy group, e.g. $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_6\text{H}_5$, isoC_3H_7 , etc.) [9]. Often they are synthesized by hydrolyzing the monomeric tetrafunctional alkoxide using an acidic or basic catalyst. The initial process follows three fundamental reactions (see Sol-gel process: silicon alkoxide reaction scheme - 1 [8]).

2. Solvent

A mutual solvent is required since most alkoxides are largely water insoluble, though the alcohol produced from the alcohol condensation reaction can be enough to solubilize the reaction system. Alcohols can act as more than simple solubilizing solvents as shown by the reverse of the second reaction in the scheme. The two main reactions to be considered are hydrolysis and condensation, which overlap. The degree of condensation and nature of the hydroxylated species define to a large extent the nature of the resulting gel. The build up of the early silica network can be represented in two dimensions (see Sol-gel process - two dimensional reaction scheme - 2., omitting the alcohol condensation/ alcoholysis reaction [9]).

3. pH and control parameters

Key control parameters are the of the water/alkoxide concentration ratio, r , the catalyst concentration which dictates the pH, solvent, temperature and the precursor itself [10, 11]. The pH and r determine the final form of the product as bulk gel, films, fibres or powders (see table 2 [8]). Fibers for instance result from using a low pH and lower than stoichiometric amount of water, or $r=1$ to 2 [12]. By contrast monodisperse spherical particles are produced at higher pH and $r=20$ to 50 [13]. Variations in the hydrolysis and condensation conditions profoundly affect the structures of the sol-gel silicates at intermediate length scales $\sim 1\text{-}20\text{nm}$ [14], (figure 6 [14]). At low pH (<4) and low r , the acid induced mechanism produces weakly branched polymeric structures unable to withstand the high capillary pressures on drying, such that shrinkage and density are high ($>1.2\text{g/mL}$) and the pore size is small ($<40\text{\AA}$). At higher pH (>6) and higher r , more compact (highly condensed) branched structures develop, dissolution and redeposition promotes interparticle strength. There is also a reduction in microporosity and an increase in the mesopore/micropore ratio. Cross-linking of the structures increases with increasing pH such that base catalyzed gels are stronger and better able to withstand the capillary forces, resulting in larger pore size ($>20\text{\AA}$), pore volume and lower density ($\sim 0.8\text{g/mL}$).

At lower pH the silicate structure continues to grow based on the three reactions previously mentioned, with the reverse reactions playing a more dominant role at higher pH (figure 7 [8]). The structural evolution of the gel depends on the mechanism of hydrolysis and condensation determined by either acid or base catalyzed hydrolysis/condensation, and restructuring due to the aforementioned dissolution-redistribution reactions and subsequent ripening process both encountered at higher pH. Further this evolution is influenced by solvent, steric and inductive effects which all influence the kinetic growth process. The early time silicate species at low pH have been identified by GCMS and ^{29}Si NMR and the distribution of silicate species at high and low pH compared (figure 8 [8]).

The nature of the alkoxide precursor has a major impact on the kinetics of the sol-gel reaction. The most commonly used silicate precursors are tetramethylorthosilicate or tetramethoxysilane (TMOS), and tetraethylorthosilicate, or tetraethoxysilane (TEOS). One or more of the alkoxy groups may be replaced by other substituents to impart more organic character, discussed in more detail in the section on hybrid xero- and aerogels.

4. Hydrolysis and polycondensation

Hydrolysis and polycondensation occur at numerous sites. Growth of these sites through Si-O-Si bonding produces a sol with a certain level of connectedness. Depending on pH these species grow into clusters which in turn aggregate via cluster-cluster aggregation or monomer-cluster aggregation. Following a critical concentration of such clusters, which may be viewed as limited networks, gelation occurs [8]. This can be viewed as the point at which the first spanning cluster appears, known as the percolation threshold, p_c , above the 50% volume level. Often p_c is of the order of 0.67 (figure 9 [15]).

5. Aging

The gel may be aged prior to drying. Aging is employed to effect a change in the final structure or properties of the gel. Condensation reactions continue long after the gel point and the aging process takes advantage of this to increase the connectivity and strength of the network, increase pore size, reduce microporosity and increase mesoporosity. The macroscopic effects of aging are polycondensation, syneresis, coarsening and phase transformation. Of these syneresis is pertinent here since it describes the shrinkage of the solid network into the liquid phase by bond formation, through condensation reactions, which causes the gel to contract. This process ceases when the strength of the solid network can withstand the capillary pressure of the liquid phase. In particulate or colloidal gels, shrinkage is governed by the balance between electrostatic repulsion and attractive Van der Waals forces. It can also change the nature of the surface. Most often these aging effects are a result of solvent exchange or

heat treatment (figure 10 [8]). At this stage the gel is a viscoelastic material which responds to a load with an instantaneous elastic strain and a continuous viscous deformation.

6. Drying - xerogels

Drying the gel effects the removal of the liquid from the interconnected pore network [14]. Stress develops in the solid network as a result of the surface tension exerted by the pore liquid as it recedes into the pore structure, which can cause cracks in the gel, becoming more acute with decreasing pore size.

$$P_c = -2\gamma_{lv} \cos \theta$$

Although cracking does not alter the physical characteristics of the gel, anymore than grinding it to a powder, it does present a problem for the fabrication of net or near net (shaped) monoliths. Drying stress also provides an insight into the rheology of the gel network. Aging can reduce the stress by either reducing the surface tension induced stress on the solid network and/or by increasing the strength or bulk modulus of the network. Drying the gel at atmospheric pressure, as for particulate or colloidal silica produces a xerogel. Some of the physical characteristics of xerogels are shown in table 3 - [8].

7. Drying - aerogels

As indicated above drying the gel at supercritical conditions of temperature and pressure eliminates the liquid-vapour interface such that $\gamma_{lv} = 0$ reducing the capillary pressure to zero also [16]. By drying the gel above its supercritical temperature and pressure, at minimal shrinkage, the resultant structure is very open, resembling closely its structure as a gel, of low density (0.1 - 0.001g/mL) and extremely porous (>98%). The structure is termed an *aerogel* (figure 11). This process was established in 1931 by Kistler [17] who was convinced that a gel was a material in which the liquid which permeated it was a continuous phase and that the solid phase was independent of the liquid. Replacing the liquid with a gas proved this point, i.e. air for liquid. Because of the solubility of silica at high temperatures it was necessary to replace, by exchange, the water in the hydrogel with a miscible solvent such as alcohol. Other supercritical fluids have been used since (table 4 [8]). Some of the physical characteristics of aerogel and xerogels are compared in table 5 - [8].

5. Gel Surface

1. Surface - xerogels

The surface of a xerogel is characterized by an abundance of -OH groups (4.9 OH/nm^2) for a typical high surface area xerogel (table 6 [5]) containing over 6% water [5]. The types of hydroxyl species are shown schematically (see Silica surface scheme - 3 [8]).

Half of the OH groups on a fully hydroxylated surface are isolated. Other surface species include unhydrolyzed alkoxide (-OR) groups, which for ethoxy groups have been measured at 3.7 OR/nm^2 . The hydroxylated surface is hydrophilic while the dehydroxylated surface is hydrophobic. Dehydroxylation diminishes the capacity of other species, such as NH_3 and ethanol, to hydrogen bond to the silica surface [8]. Cyclic species resulting from the condensation of silanol groups can significantly affect dissociative chemisorption of surface hydroxyls. The general stages of dehydroxylation are shown in figure 12 -[8]. Cyclic trisiloxanes appear around 200°C [19] and cyclodisiloxanes at 650°C [20]. Surface energies increase from 0.15 to 0.28 J/m^2 with increasing dehydroxylation. The surface chemistry of the hydroxylated silica surface with other species is dominated by hydrogen bonding. The high surface area and general accessibility of silica form the basis for the use of silica gels in the areas of separation and catalysis, especially in the dehydroxylated form.

2. Surface - aerogels

Aerogels produced by the high temperature process (e.g. ethanol, $T_c = 240^\circ\text{C}$) are extensively esterified, due to the interaction of the alcohol with the surface silanols by reaction 2 above, yielding a hydrophobic surface. Conversely aerogels produced by a low temperature process (e.g. CO_2 , $T_c = 35^\circ\text{C}$) have a predominantly hydrophilic surface [18].

6. Chemical modification of xerogels and aerogels

Aerogel and xerogel surfaces can be chemically altered in two ways: 1. surface modification (subsequent to gelation and drying) and 2. by incorporating functional groups into the gel precursor or as the gel matrix develops. Both of these methods form the basis for catalytic sol-gel materials and the second method the basis for making multicomponent gels. Modification of the surface can be achieved by attaching : i) organic ions ii) SiO-C linkages and silicic esters and iii) Si-C bonds as organosilicon groups [5]. The adsorption of chemisorbed organic groups can make silica surfaces/ particles dispersible as organosols [21]. In the same way the surface polarity can also be influenced. Esterification with glycol produces silica particles soluble only in polar organic solvents but not in hydrocarbons [22]. Esterification of the same particles with hexamethylene glycol however, with the -OH groups turned inwards towards the silica surface, makes the material soluble in hydrocarbons [23]. Complete coverage of the surface or complete esterification is not required to bring about

this effect. This behaviour can be achieved by as little as a monolayer coating of the surface with a chosen compound resulting in profound changes in surface properties.

1 Silylation

Silylation of the surface produces a still more stable organophilic surface. A coating of methylsilyl groups allows the treated silica to be dispersed in a multicomponent alcohol and water (<3%) mixture by wetting alone [24]. Even at high temperature the surface is extremely resistant to water owing to the non-hydrolyzability of the $\text{CH}_3\text{-SiO}$ surface. Other substituents investigated include nitroalkyl, chloroalkyl, and alkoxyalkyl [25]. The organic substituent, R in SiOR , can also be an acidic component such as a mercapto, phenolic, sulphonic, phosphonic, or carbamic group; R can also contain a fluorocarbon, an unsaturated or an amino group to mention a few of the main possibilities. Silanization, where the surface is hydrophobicized by hexamethyldisilazane is a common practise in gas chromatography. It reacts with the SiOH group to produce $\text{SiOSi}(\text{CH}_3)_3$ on the surface liberating ammonia [26]. A partial list showing some of the surface reactions on silica is presented in figure 13 - [5]. The surface be derivatized with trimethylchlorosilane [27, 28] which lowers the contact angle and can further react with ethylene or butadiene as a means of attaching alkyl groups [29].

2. Introduction of metal oxides and metal ions

The silica surface is weakly acidic but can be modified by the addition of alumina, by treating with sodium aluminate at pH 9 - 10, to produce an aluminosilicate. The ensuing surface is strongly acidic. Exchange of the sodium ions for ammonium ions, and heating gives an acidic cracking catalyst. Heating such aluminosilicates in water at constant pressure, of course produces zeolites. Other polybasic cations such as iron, thorium, beryllium and lanthanum can be adsorbed by silica to give a positively charged surface which can act as an anion exchange medium. These surfaces irreversibly adsorb phosphate ions, and then act as a cation exchanger, capable of separating metal ions such silver, copper (2^+), iron (2^+) and calcium [30]. Using silica as the support for such cationic exchange materials illustrates the effective use of the high surface area and its wide pores for efficient performance. The separation of aromatic amines can be enhanced by incorporating cadmium ions on the silica surface as coordination complexes. Carboxyl substituents of long chain fatty acids can effectively adsorb chromate ions.

3. Introduction of organic components

Organically linked ion exchange sites leading to Si-C bonds are exemplified by grafting styrene, acrylic acid, vinylpyridene or vinylphosphonic acid followed by

the introduction of ionic groups by sulphonation, chloromethylation or ammination [31]. Refluxing porous silica (surface area = $600\text{m}^2/\text{g}$) with (3-chloropropyl)trichlorosilane in xylene, followed by exchange of the 3-chloro groups with dibutyl amine at 140°C produced an amminated silica surface with an exchange capacity of 0.5meq/g [32]. This material can adsorb carbon dioxide from air and in the presence of moisture, sulphur dioxide and hydrogen sulphide [33]. Aminopropyl groups can be attached to the surface by reacting silica with (3-aminopropyl)triethoxysilane [34]. Subsequent treatment of the surface enables the chelation of copper and other heavy metal cations to a hydroxyquinoline complex down to extremely low concentrations.

7. Adsorption

1. Hydroxylated surface and hydrogen bonding

Some of the foregoing examples will be further described in this section as the adsorption on silica is more generally discussed. Hydrogen bonding defines the surface chemistry of hydroxylated silica, through the interaction of the surface hydroxyls and the electronegative atoms/pi electrons of the adsorbate. In general the higher the hydroxyl concentration the greater the adsorption. The adsorption of polar or aromatic molecules through pi-bonding occurs most strongly on silanol groups which are not hydrogen bonded to neighboring hydroxyls. Partially dehydrated silica at 500°C ($2.7\text{ OH}/\text{nm}^2$, $\sim 50\%$ coverage) adsorbs one $\text{C}_6\text{H}_5\text{NH}_2$ (pyridine) molecule per hydroxyl [35] and the same is observed for ammonia [36]. Adsorption on silica-alumina is not as strong, indicating fewer OH per nm^2 . The increase in the cis-trans ratio from 1 to 1.9, of dichlorobenzene on silica suggests the form which displays the highest number of hydrogen bonds is preferred (see cis-trans surface effect scheme - 4 [37]).

2. Amine adsorption

Adsorption of amines on the surface, including ammonia, is not simple and may combine both chemical and physical adsorption. e.g. ammonia on silica is irreversibly adsorbed below 70°C [38]. The mechanism certainly changes with the strength of the base and the pH of the solution, such that hydrogen bonding occurs at neutral pH whereas salt formation is found at higher pH for long chain amines. One study found that diethyl, mono- and dibutyl amines formed monolayers at low relative pressures (p/p_0) of 0.01 [39]. The degree of hydroxylation of the surface influences the degree of adsorption for polar molecules and polyunsaturated hydrocarbons, becoming maximal for a fully hydroxylated surface. Isolated, freely vibrating, hydroxyls on a dehydrated silica surface (free of adsorbed water) effect the strongest adsorption of organic

compounds [40], with aromatics attaching in a 1:1 ratio as for pyridine. Drying at 175°C is optimal, in terms of removing adsorbed water while preserving the maximum number of hydroxyl groups. A fully hydroxylated surface is better at providing multiple adsorption sites that fit the adsorbate of multipolar or multi-unsaturated molecules.

The interaction between the silica surface and a variety of adsorbates has been investigated and the following order of adsorption strength found [41]:

pyridine > CH₃CN = benzene = CH₃NO₂ > Ar, N₂, cyclohexane

The relative effectiveness of hydrogen bonding adsorbates is shown in table 7 - [5]

The adsorption of amines on the silica surface has been studied largely by Russian workers. Mischenko and Neimark [42] found that di- and triethylamine were irreversibly adsorbed on poly(chloromethyl)siloxane xerogel, and the amount increased as a function of temperature. Some of the adsorbed material could not be removed even under vacuum at 150°C. Mischenko [43] extended the study to include polymer xerogels with methyl, vinyl and phenyl groups in place of the chloromethyl, noting a donor-acceptor interaction between the amines and the surface silanols and organic radicals at low p/p₀. Neimark and Mischenko [44] went on to find that contrary to convention, diethylamine adsorption increased with decreasing =SiOH and =SiCH₃ groups on the surface of poly(methylsilane) xerogels. Later these workers [45] discovered that diethylether and diethylamine adsorption increased on poly(vinylsiloxane), when functional groups of the same chemical nature predominate on the surface of the xerogel. Presumably the more polar the siloxane substituent the greater the uptake of these polar adsorbates. Another member of the Russian group, Slinyakova [46], interpreted the order of adsorption of several of adsorbates, including amines, on the basis of surface acidity. Adsorption on poly(titanomethylsiloxane), containing 0.7% and 2.1% TiO₂ respectively, and poly(methylsiloxane) xerogels showed the adsorption increased in the order:

(C₂H₅)₂ >> CH₃CN >> hexane >> CH₃NO₂

The overall level of adsorption was greater on the higher titania containing xerogel.

More recently the adsorption of aniline, by an insertion process, on vanadia xerogel has been studied [47]. The reaction is facile with the aniline polymerizing on exposure to oxygen. In a related study aniline was inserted and polymerized inside a molybdenum trioxide gel network, using a concomitant ion-exchange - polymerization approach, in the presence of an external oxidizing agent [48].

3. Other organics

The adsorption of alcohols, hydrocarbons, including aliphatics, cyclics, aromatics, carboxylic acids, fatty acids and phenols amongst others from non-aqueous solvents have been studied. The degree to which one organic molecule can be displaced from another on the silica surface depends on three factors: 1. the strength of the hydrogen bond (see table 7 [5]), where the hydrogen bonding of the OH is stronger with a weak base than the O atom of an ether/ keto group [41]; 2. the relative proportion of hydrocarbon to polar groups in the molecule (surface activity); 3. the number of electron donors per molecule. Few polar compounds of low molecular weight are known to be very strongly adsorbed from aqueous solution, because of the competition of water for the site, with the exception of nitrogen bases.

4. Metal ions

The adsorption of metal ions (table 8 [5]) has been extensively studied, including univalent and divalent alkaline and alkaline earth metals and polyvalent metal cations such as Al, Fe, U, Pu and Cr. Surface adsorption of Fe^{3+} , Al^{3+} , and Cr^{3+} is strong at low pH [49, 50]. Many ions are strongly, often irreversibly adsorbed/held by forces in addition to ionic attraction. When a metal ion is strongly complexed it can act like a cation of a strong base and moving close to the surface induce negative charges (SiO^-) equal in number to its own charges and releasing an equivalent number of H^+ . This effect was reported by Vydra and Markova [51] for ethylenediamine complexes of Ag^+ , Zn^{2+} , Cu^{2+} , Co^{2+} , and Co^{3+} . Adsorption of polybasic ions is thought to be irreversible, proceeding through chelation by the surface silanol groups which can replace the coordinated water molecule of the ligand or complex [52]. This was supported by the finding that in the adsorption of $\text{Cu}(\text{NH}_3)_4^{2+}$, the NH_3/Cu ratio was less than 4 [53]. The silica surface can also undergo numerous non-ionic reactions with a variety of compounds often forming stable coatings (figure 13 [5]).

In terms of a hydrophobic surface, silica treatment reactions may be summarized:

1. Adsorbed organic cations: nitrogen bases, quaternary ammonium ions
2. Adsorbed polyvalent metal ions attached to long chain fatty acids
3. Esterified silanol groups
4. Organosilyl coatings
5. Adsorbed linear polymers with hydrogen-bonding side groups

Some of the most resistant and stable hydrophobic coatings include polymethoxysilane and surface $(\text{CH}_3)_3\text{SiO}-$ groups [104].

8. Organic-Inorganic hybrids

The incorporation of an organic component into a inorganic matrix can change the structural and surface properties of the inorganic quite significantly. This has some important implications, not least in the area of adsorption.

1. Ceramers

Ormocers, ormosils or ceramers are terms often used to describe the hybridization of a metal oxide, usually silica, with an organic substituent/group/polymer to produce the corresponding xerogel or aerogel. This procedure was pioneered by Schmidt who recently reviewed the field [105]. The approach has also been expanded to include the non-reactive introduction of polymers into an inorganic matrix, described as interpenetrating networks (IPNs) [106]. Chemical modification [107] of metal oxide xerogels and aerogels is desirable to tailor either the bulk, surface or both, to take advantage of the properties of each component. Consideration of the bulk properties of each component is required, in particular the nature of the interface of the nanometric scale phases and the timing of the addition of each component, in order to form a successful hybrid.

2. Xerogel hybrids

A styrene-3-(trimethoxysilyl)propyl methacrylate copolymer was reacted with TEOS in acid/THF solution [108] producing a covalently bonded composite involving both surface and bulk silanols. The polymer chains were uniformly distributed and the resulting properties, refractive index, density and hardness (measured as a function of increasing TEOS content) were intermediate between those of the pure components in an optically clear composite. Many other polymers have been incorporated into a hybrid network with TEOS, such as poly(methylmethacrylate) [109], poly(vinylacetate), poly(vinylpyrrolidone) and poly(vinyl N,N-dimethylamide) producing transparent films demonstrating the absence of macrophase separation. Hydrogen bonding between the inorganic and organic components is the key to reducing the separation. Other principles for linking organic to inorganic components can be summarized (figure 14 [110]). Functional groups/substituents can be categorized as network formers, if they are non-polymerizable ($-C_6H_5$, $-C_2H_5$, $-(CH_2)_nNR_2$, $-COOH$). Conversely they are termed network modifiers if they contribute to the network by reaction, usually hydrolysis (acetylacetonate $CH_3COCHCOCH_3$, amino, carboxyl, cyano, aldehyde, olefin or epoxy) [111]. Modification of the precursor can be carried out to alter the nature of the ensuing hybrid. The effect of the organic substituent in the precursor can impact the structure quite dramatically. Xerogels formed between TEOS and methyltriethoxysilane (MTEOS) or dimethyldiethoxysilane (DMDEOS) [112] showed a considerable increase in surface area, from $400m^2/g$

to 800m²/g, as a function of increasing MTEOS content, and 600 to 700m²/g as a function of increasing DMDEOS content, under acid conditions. Conversely there was a dramatic decrease in surface area when each hybrid was formed under basic conditions from over 800m²/g, at the 70% level of MTEOS, and at the 40% level of DMDEOS to 1m²/g. The two methyl groups of DMDEOS accounting for the same effect at almost half the level in the hybrid. Hydrophobicity was also increased in all cases by the incorporation of the methyl substituents (in DMDEOS and MTEOS).

3. Aerogel hybrids

Aerogels have also been organically modified by mixing TMOS with methyltrimethoxysilane (MTMOS), again producing a hydrophobic surface [113]. Since the hydrolysis of TMOS is much faster than that of MTMOS it means that the TMOS gel network will be largely formed by the time the hydrolysis of MTMOS is significant. This translates into MTMOS reacting with the only hydrolyzable species available, the surface silanol groups on the TMOS. As the proportion of MTMOS increases the aerogel shrinkage increases, though paradoxically the bulk density decreases due to the decreasing number of surface OCH₃ groups. Surface areas of these hybrid aerogels ranged from 540 to 680m²/g. Subsequently other non-reactive substituents were studied by this group [114] where CH₃, phenyl and butyl substituted TMOS (RSi(OCH₃)₃) was reacted with TMOS as were the dimers of the form (CH₃O)₃Si-Y-Si(OCH₃)₃, where Y = C₂H₄, p-C₆H₄, and C₆H₁₂. The same workers [115] went on to study the pyrolysis of the phenyl substituted aerogel, in which nanometre sized carbon structures (coated clusters) were generated, which only partly coated the primary aerogel particles (figure 15 [107]). This topic has been comprehensively described by Schubert [107], including the concept and structural characterization of "coated clusters". The ability to permanently hydrophobize the surface by incorporating non-reactive alkyl or aryl groups into the inorganic matrix at an optimum 20% precursor level was emphasized.

9. Non-silica metal oxide xerogels and aerogels

1. Non-silica precursors

Metal oxide precursors for metals other than silica abound, though the study of silica xerogels and aerogels dominates the field. Other oxide systems have been thoroughly described by several authors, which include group one, two three and four gels from metal alkoxides [116], transition metal oxides from the corresponding metal alkoxides or inorganic salts in aqueous solution. The latter includes nitrates, chlorides, carboxylates and acetates. Metal alkoxides [117] are however the most versatile of precursors in the sol-gel synthesis of metal oxides. They are known for almost all of the transition metal elements and the lanthanides. Alkoxides and the corresponding xerogels/ aerogels of the near

transition metal elements are better known [118]. Reactivity, degree of oligomerization and polymerization vary depending on a number of factors such as the nature of the metal atom (size, electropositivity, etc.), degree of branching of the alkoxy precursor, the solvent and solute concentration. The electronegativity of silicon means that most non silicon alkoxides are more reactive towards water.

3. Transition metal oxides

The number and stability of transition metal alkoxides decreases from left to right across the periodic table. The more routinely studied alkoxide, non-silicon derived gels include titanium, zirconium and aluminum. Often the high reactivity of these alkoxides can be controlled by using chelating ligands such as glycols, organic acids and, in particular, β -diketones such as acetylacetone. Alcohol interchange is faster for transition metal alkoxides than silicon alkoxides, the rate increasing as the steric hindrance of the alkoxide substituents decrease, i.e. from tertiary to secondary to primary groups [118].

Other well known gel systems include vanadium, from sodium metavanadate, chromium oxide from the chloride, nitrate salts, sulphates, acetates and alkoxides of triethoxyethanol. Manganese from diethoxyethanol, iron from Fe^{3+} salts, cobalt from the acetate or triethoxide, nickel from the tartrate and acetate and copper from the tartrate, nitrate, sulphate and acetate have also been used.

10. Multicomponent gels

The preparation of multicomponent gels [119-122] (table 9) is especially suited to the sol-gel process, provided that due attention is given to the difference in reactivity of the precursors. Several techniques have been developed to overcome the different hydrolytic rates such as sequential precursor addition, in order of increasing reactivity, or modification of the metal oxide precursor substituents.

An Al, Cr, Zr, Si and Na oxide system was prepared by Gotardi [123] which demonstrates the power of the sol-gel technique. More commonly however the binary and ternary systems are synthesized that also occur naturally such as Al_2O_3 - SiO_2 (mullite), B_2O_3 - SiO_2 (borosilicate) and TiO_2 - SiO_2 , used as low thermal expansion glasses, SiO_2 - TiO_2 - ZrO_2 and SiO_2 - Al_2O_3 - B_2O_3 [8].

11. Sol-gel derived catalysts

1. Aerogels

One of the early innovators in the use of the sol-gel method was S.J. Teichner [124]. His group focused particularly on the preparation of aerogel and xerogel catalysts from alkoxide precursors, in both supported and unsupported form [125]. He along with Peri [126] are credited with preparation of aerogels based on silicon alkoxides as opposed to the original method of Kistler [127, 128] which used silicic acid or sodium silicate. Teichner's approach simplified the whole process by making use of the silicon alkoxide's solubility in alcohol at the precursor, reaction and supercritical drying stages. Formerly water was the solvent which dissolved silica at high temperatures (T_c). Kistler knew this and had to exchange the gel with alcohol, but this was very time consuming. Like Teichner 30 years later, he was also interested in the use of aerogels as catalysts. He recognized that the high surface area ($700 - >1000\text{m}^2/\text{g}$), coupled with large pores (up to 600nm) and high pore volume ($\sim 20\text{ mL/g}$; $>90\%$ porosity) would provide a very active and accessible (continuous) surface. One of these early catalysts was thoria aerogel, from thorium nitrate, which converted aliphatic acids such as acetic acid to ketones. Significantly, the aerogel catalyst was superior to the conventional thoria (hydrogel-xerogel) catalysts [129].

2. Aerogel surface characteristics

This higher activity and selectivity is a key feature of aerogel catalysts, over their conventional counterparts. In addition they are often more resistant to deactivation. Teichner found the catalytic properties of aerogel catalysts to be more diverse than the corresponding xerogel [130], in studies that have produced over 50 publications on the subject. The higher activity and selectivity of aerogel catalysts is due to the nature of the active components in the aerogel itself. A good example is the binary oxide aerogel of $\text{Fe}_2\text{O}_3 - \text{SiO}_2$ which has a surface area of $800\text{m}^2/\text{g}$ and an activity 2 to 3 orders of magnitude greater than the conventional reduced Fe_3O_4 catalyst ($10\text{m}^2/\text{g}$). The work in this area has been reviewed by Teichner [131]. He also observed that the mixed oxide aerogels exhibited much higher surface areas than the pure components [132]. For example the surface area of $\text{NiO} - \text{Al}_2\text{O}_3$ binary oxide aerogel was measured at $710\text{m}^2/\text{g}$ for a 5:1 ratio of Al_2O_3 to NiO . The surface areas of the pure component aerogels were no greater than $600\text{m}^2/\text{g}$ for Al_2O_3 and $200\text{m}^2/\text{g}$ for NiO . This phenomenon is most strikingly demonstrated in the binary oxide aerogel of $\text{MgO} - \text{ZrO}_2$, where the surface area of ZrO_2 is around $400\text{m}^2/\text{g}$ and for MgO around $300\text{m}^2/\text{g}$. The surface area of the mixed oxide aerogel is $800\text{m}^2/\text{g}$ and is attributed to the probable formation of an amorphous solid solution.

3. Some reactions of aerogel catalysts

$\text{NiO} - \text{Al}_2\text{O}_3$ aerogel catalysts are very selective for the partial oxidation of isobutene to methacrolein in 66% yield. The conventional NiO on alumina catalyst is well known for the complete oxidation of isobutene and other olefins.

The elimination of secondary oxidation is also observed in the supported NiO on alumina aerogel catalyst [133].

Interestingly in the ternary mixed oxide aerogel of NiO - Al₂O₃ - SiO₂ the surface area and micropore volume decreases with increasing alumina content while the macropore volume increases [131]. This suggests that alumina is responsible for macropore volume and silica for the micropore fraction (table 10 [131]).

Silver supported on silica aerogel was shown to have increased mesoporosity compared to the xerogel form, though the xerogel had a higher microporosity. The silver was reduced from the Ag⁺ state on the aerogel surface [134]. Other contributors in the field of aerogel catalysts include workers at Allied Signal who developed chromia catalysts with high surface area and pore volume [135]; and palladium on alumina aerogel amongst others [136]. The group of Hair and Droege [137] recently reviewed the application of aerogel derived catalysts, where the catalytically active metal is incorporated into the framework to effect NO_x reduction (Cu-SiO₂ and V-SiO₂), the oxidation of volatile organic compounds (VOCs) (Zn-SiO₂, ZrO₂) and partial oxidation of methane (V-SiO₂, TiO₂, amongst others). These workers have also studied these reactions using palladium or platinum on silica aerogels and the partial oxidation of hydrocarbons [138].

The reduction in the level of NO_x (de-NO_x) is a much studied reaction. NO_x can either be reduced directly on the catalyst surface or by using a reducing agent in the gas stream such as NH₃, over a vanadia-titania aerogel catalyst. Teichner [139] had suggested using a Fe-Cr-Al aerogel catalysts for the de-NO_x process with a subsequent study showing high catalytic activity. Later work [140] showed a marked increase in the surface area and pore volume when small amounts of iron or chromium were incorporated into alumina. The higher activity of the aerogel compared to the equivalent xerogel was attributed to the higher diffusivity of the reactant gases due to the larger pore size and pore volume [141]. Resistance to coking was demonstrated by a Ni on alumina aerogel catalyst in the dry reforming of methane [142]. Ultraviolet irradiated titania-silica aerogels have been used to photocatalytically degrade aqueous cyanide species to carbon dioxide and nitrogen [143]. Higher catalytic activity with increasing silica content was observed for the oxidation of CN⁻ in ferric cyanide solution. The catalyst was re-used several times with no detectable loss in activity.

4. Xerogels

Xerogels have also found application as catalysts. A novel chemisorbed alumina on silica xerogel catalyst [144] was found to produce a gasoline fraction from methanol in much the same way as the original ZSM5 homogeneous aluminosilicate zeolite catalysts developed by Mobil. Pore size was of the order of 1nm, which is crucial to the formation of alkanes, alkenes and aromatics by a combination of Bronsted activity and shape selectivity. Another group that has

made a large contribution to the area of supported metals on xerogel, mainly silica catalysts, is that of Lopez and Gonzalez [145-147]. They have investigated the preparation of ruthenium, platinum and palladium amongst others on silica xerogel. Key to the successful dispersion of the metal clusters/crystallites on the xerogel surface was the matching of pore size to crystallite size by a somewhat synergistic effect, of the order of 4nm.

12. Non-oxide organic and carbon aerogels

Organic aerogels result from the reaction of organic precursors which form a polymeric network [148] in a way that resembles their inorganic metal oxide counterparts sufficiently to be classed as xerogels. Supercritical drying of these organic xerogels produces aerogels.

1. RF aerogels

Organic aerogels have been made from a variety of precursors, though the most studied are based on the base catalyzed reaction between resorcinol and formaldehyde (RF) in water. The pore fluid is then exchanged for acetone as an intermediate step before exchanging again for carbon dioxide. The CO₂ exchanged xerogel can be supercritically dried at low temperature, 31°C (table 4) producing a dark red but transparent monolith. Like the inorganic analogs, a large degree of control can be exercised over the structural properties of the gel. For instance, varying the resorcinol to catalyst ratio, R/C, changes the particle size of the polymer which effects both density and surface area. The average atomic number, Z of the formed polymer is lower than that of inorganic aerogels. The preparation procedure and general details in the fabrication of a resorcinol-formaldehyde aerogel has been discussed in several articles, which the group of Pekala [149] dominates.

2. RF reaction mechanism and growth

Resorcinol (dihydroxybenzene) is a trifunctional compound which reacts with difunctional formaldehyde, mixed in a 1:2 molar ratio in water under basic conditions (figure 16 [150]). A highly cross-linked polymer network characterized by methylene and methylene ether bridges forms [150, 151], evolving from the condensation reactions between the resorcinol-formaldehyde (RF) monomers, leading to gelation, via cluster-cluster aggregation. The intermediate xerogel has been found, in this laboratory, to be highly microporous with a density of ~0.5g/mL [152]. The aerogel itself is considerably less dense, ~0.07g/mL, at 5%, weight solids content (based on weight of reactant resorcinol and formaldehyde) and a R/C ratio of 300. Resorcinol can be substituted by its isomers, catechol and hydroquinone. The reaction mechanism follows that of the well known resin producing phenol-formaldehyde polymerization reaction, with electrophilic substitution of the formaldehyde ion at the 2, 4 and 6 ring positions. The ring is

activated at these positions by the base abstraction of hydrogen from one of the hydroxy groups, to form a resorcinol anion or oxide ion. Activation is strongest at the 2 and 4 positions, where the negatively charged oxide ion is most stable, due to inductive effects. The higher electron density at these positions supports this. Steric hindrance of the 2 position however means that reaction takes place preferentially at the 4 and 6 positions [153]. Once the hydroxymethyl-resorcinol intermediate is established, polymerization between the hydroxymethyl groups begins to form methylene and methylene ether bridges. The methylene ether bridges can also disproportionate to form methylene bridges and the by-product formaldehyde [154]. RF clusters develop (30 - 200Å) from these initial cross-linking reactions and begin to aggregate at about 60% consumption of reactant formaldehyde, proceeding towards gelation.

Cluster size of the colloid like particles depends on the catalyst concentration, increasing with increase in base. Early time consumption of resorcinol produces clusters covered in hydroxymethyl groups. The size of the clusters is a function of the R/C ratio, because of the resorcinol anion dependence on base catalyst concentration. Cluster growth proceeds between uncharged monomer (RF) and cluster, on account of the electrostatic repulsion between charged clusters, increasing the number of available reactive sites (functionality) which in turn consumes more monomer. Following consumption of resorcinol the remaining formaldehyde reacts with the sites on the surface of the clusters producing more hydroxymethyl groups, analogous to the synthesis of starburst polymers. Inter-cluster cross linking now proceeds leading to a gel through microphase separation and incompatibility, and ultimately phase separation of the network from the pore fluid. The particulate microstructure and morphology of the gel is largely determined by the R/C ratio [155]. In general the gelled particulate structure is often described as having a "string of pearls" morphology of interconnected colloid like particles or polymer chains with diameters of ~10nm, characterized by pores of <50nm, and high surface area, 600 - 1000m²/g. Drying at ambient pressure produces the xerogel [152, 156].

pH is an important parameter, and although it does not control the microstructure to the same extent as for a metal oxide gel, it needs to be around 7 to prevent excessive shrinkage. Higher pH increases cross-linking, which for RF aerogels translates into higher density, unlike the metal oxide aerogels.

3. Carbon xerogels and aerogels

Pyrolysis of the RF xerogels or aerogels in an inert atmosphere produces vitreous carbon xerogels and aerogels, which retain the same interconnected morphology as the non-pyrolyzed precursors [157]. Pyrolysis does however modify the particle size, surface area and particle interconnections. It also increases the thermal and electrical conductivity, producing in effect a glassy carbon [158]. The carbon xerogels and aerogels are black in color and opaque.

They are also stronger and stiffer than the RF xerogels or aerogels. Pyrolysis causes up to 70% shrinkage and a mass loss of some 50% [150, 152]. Densities are therefore higher than the RF equivalents.

In summary it may be said that the polycondensation of resorcinol with formaldehyde under alkaline conditions follows a sol-gel pathway in which surface functionalized polymer clusters are formed. The covalent cross-linking of these clusters produces gels which may be of high (xerogel) or low density (aerogel) depending on the drying procedure. Both forms have continuous porosity with cell/pore sizes less than 100nm. Their microstructure is composed of interconnected colloidal-like particles with diameters of 30 - 150A.

4. Carbon aerogel catalysts

The large pore, high surface area and controllability of pore/particle size of RF and RF carbon aerogels makes these materials good candidates for catalyst supports. The nature of the surface makes RF aerogels and RF carbon aerogels an interesting departure from the inorganic derived equivalents.

Platinum (1-10%) on RF carbon aerogel was prepared [159] by exposing the intermediary RF xerogel to the appropriate concentration of a dilute solution of chloroplatinic acid in dimethyl formamide. The exchange took place over several days to ensure a uniform distribution. The hexachloroplatinate - RF gels were heated to 140°C for 16-24 hours in an excess of the chloroplatinate solution to effect reduction of the surface salt to platinum "islands" that measured 5-250nm at 10% platinum loading. The BET surface area was measured at 765m²/g. The gels were supercritically dried and subsequently pyrolyzed. The catalyst was used to selectively reduce NO with ammonia in air. Conversion of NO was 12% at 250°C, comparable to a conventional platinum on silica catalyst. This value also compares well with the that of 20% for the V-SiO₂ and Cu-SiO₂ aerogel catalysts discussed earlier, bearing in mind the higher temperature used of >400°C.

5. Other carbon xerogels and aerogels

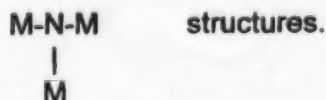
High surface area, highly porous carbon aerogels have also been made from other organic xerogel precursors [150]. These include the isomers of resorcinol, hydroquinone (1,4 dihydroxybenzene), catechol (1,2 dihydroxybenzene) and phloroglucinol (1,3,5 trihydroxybenzene), of which only the latter produces a comparable aerogel. Polyfurfuryl alcohol, polyacrylonitrile (PAN), polyvinylidene (PVD) and polyvinylidene chloride (PVDC), polyvinylidene fluoride (PVDF) and their various mixtures, in addition to the original phenol-formaldehyde resin are other precursors. Reticulated vitreous foams are derived from open cell polyurethane infused with furfuryl alcohol [157, 160].

Melamine-formaldehyde (MF) xerogels and aerogels are of interest due to their optical clarity and amine activated melamine precursor, where hydrogen abstracted NH_2 groups attached to the ring activate it in a way directly analogous to the OH groups in resorcinol [161]. However the six hydrogens attached to the three N atoms, make melamine a hexafunctional monomer capable of reaction at each of the three NH_2 groups. Moreover using melamine is a good way to introduce nitrogen at the precursor level, into the polymer matrix. The reaction chemistry is similar to that for RF, with the important distinction of substituting diaminomethylene bridges in place of methylene ethers.

Carbon surfaces have been introduced to inorganic xerogel and aerogel surfaces as mentioned previously, in the modification of silica aerogel by replacing SiOH groups with non-reactive SiR substituents for instance. At the Jet Propulsion Laboratory [162] inorganic- organic hybrids have been made by treating the surface of silicate with furfuryl alcohol, optimized at a 1:1 ratio and pyrolyzing at 600°C to generate a stable hydrophobic surface. This adsorbent is very effective for adsorbing small molecules in the 3-6Å range, due to the molecular sieve like properties of the pores of the carbon surface on the zeolitic support. Similar composites were studied by Kamiya [163], who in a manner similar to that described by Schubert above, took MTES as the gel precursor, but with the direct aim of pyrolyzing the gels (1100°C) to give a porous carbon lined surface with an overall carbon content of 25-30%. High surface area silica xerogel and aerogel composites have been fabricated by mixing activated carbon with a developing silica xerogel network derived from the polycondensation of TMOS [164]. The carbon was found to increase the surface area of the silica gel and made the surface hydrophobic. The pore structure of the xerogel composites was dominated by carbon while that of the aerogel was controlled by the silica. Work in this laboratory using TEOS as the silica precursor to produce carbon-silica composite xerogels [165] confirmed that the pore structure was dominated by carbon. These composites were, under the right conditions, made as monoliths which would make them attractive as preforms for a variety of shapes.

13. Nitrides

This class of materials forms an interesting subset of the inorganic metal oxide sol-gel category, in that bridging M-O-M atoms are replaced by



This can be achieved by modifying the metal oxide surface by ammonolysis or by incorporating the nitrogen (nitride) into the network at the precursor level. Bulk

modification in this way, by gas/liquid, is possible because of the highly exposed surface and accessibility, owing to the continuous porosity (a silica gel of area $850\text{m}^2/\text{g}$ has 65% of its silica on the surface [8]). Schemes that take the ammonolysis route are shown in figure 17 - [8]. Adsorption due to a strong Lewis acid interaction applies to electrophilic metals such as boron or aluminum in scheme A. Scheme B is relevant to silica where the lewis acidity can be expected to increase by dehydroxylation. Scheme C applies to higher temperatures, $>650^\circ\text{C}$ and scheme D to metal alkoxides with amino compounds such as ethanolamine. In the presence of hydrogen or carbon, introduced by way of alkoxide or acetate groups for instance, the dehydroxylated silica surface can be reduced by ammonia at higher temperatures. All schemes lead to amines or imines. Boron has been found to be more susceptible to nitridation than silica, in the nitridation of borosilicate, proceeding by dissociative chemisorption. Generally higher temperatures ($>600^\circ\text{C}$) are required to achieve higher than 5% nitrogen incorporation. Between 700 and 1000°C up to 40% nitrogen can be incorporated.

Significant nitridation of MTES originated fibres, compared to TEOS base fibres has been observed above 600°C , where the CH_3 group is instrumental in promoting the reaction (figure 18 [8]). Boron nitride aerogels exemplify nitrogen incorporation at the precursor level in producing a non oxide ceramic. The low density of boron nitride aerogel, low thermal expansion and average atomic number couple with high chemical resistance bears similarity to carbon aerogels

Amorphous or crystalline hexagonal boron nitride can be made from poly(borazinylamine), supercritically dried, and subsequently pyrolyzed to give a low density boron nitride aerogel. These aerogels retain relatively high surface area at high temperatures ($\sim 500\text{m}^2/\text{g}$ at 1000°C) and surprisingly almost 50% of the pore volume is in the micropore region [166].

14. Aerogels and Xerogels as Filters

Interest in xerogels and aerogels as filters and separation media has intensified over the last decade or so. The high surface areas and pore sizes in the micron (aerogels) to nanometer range, present as continuous porosity (>90% in aerogels), coupled with their inherent surface activity (see section 5) makes them ideal candidates to act as filtering materials. They can be used for the filtering/separation of a variety of particles including gaseous and liquid compounds, metal ions and their complexes. The use of fibres in various forms such as glass fibre, fluoropolymer staple fibres, micrometal fibres amongst others have found traditional and emerging uses as filtration media [167]. Aerogels are now considered in many respects to be an extension of the application of fibrous materials to filtration. Interestingly the applicability of aerogels to act as microporous filters was recognized by Peri [168], in a patent, in 1969, who made self sustaining crack free sheets of aerogel which could also act as a catalyst support and, for that matter as we now know, as a catalyst itself.

Cooper [169] in a detailed theoretical study, considered aerogels highly suitable as filters, primarily due to the low pressure drop associated with them. Resistance to flow (pressure drop) and particle removal efficiency are the two most important factors when considering any material for use as a filter. Efficiency represents the benefit of the filter and resistance the cost. The ratio of the collection efficiency to the resistance or pressure drop is termed the quality factor which can be used as a figure of merit. It is an intrinsic measure so that it is the same for any thickness for any filter material. The higher the quality factor the better. This enables aerogels to be compared with other filter materials. The quality factor for aerogels is unusually high in comparison with other common fibrous filter media. This is due to the small size of the fibres which comprise the typical aerogel. An analysis based on single fibre efficiency, calculated for a fan model filter under specific conditions, showed that as the fibre diameter decreases the single fibre efficiency increases. The high porosity of the aerogel imparts a low resistance to flow. Consequently the quality factor increases on both accounts and this leads to equivalent collection efficiency at lower pressure drop (resistance) or higher collection efficiency at the same pressure drop associated with thicker fibre materials. The rigidity of aerogels is viewed as advantageous in that they would be self supporting and their translucency may indicate the extent to which they have been exposed.

Attia has devoted considerable effort to the study of aerogels as agents for the capture of various gaseous pollutants. The removal of NO_x , CO, CO_2 , SO_2 and H_2S on MgO containing CaO aerogels has been quantified [170]. Very high removal (adsorption) levels were measured (>90%) for all of these gases when the aerogel was steam activated prior to use. The water vapour was thought to increase the number of surface hydroxyl groups and as such the surface activity. H_2S removal, initially at 90% fell to 40% with time, apparently due to the

presence of water vapour. Operating at higher temperature in the absence of any steam activation would improve the adsorption of H_2S . Small (200mL) and large (1500mL) monoliths and granulated aerogel pieces (<5mm) were tested. Removal of the gaseous pollutants was by a chemisorption process occurring on the gel surface. The ability to engineer aerogels to different forms, sizes and chemical compositions, in order to remove pollutants from air, is a decided advantage [171].

An aerogel mesh contamination collector or getter was developed for the collection of nanoscale particles, primarily for the microelectronics industry [172, 173]. A metal mesh matrix was coated with a low-density porous aerogel, where previously bare metal mesh matrices alone were used as getters. In the composite getter the low-density aerogel coating protects the enclosed metal matrix from ablation and also attracts and holds the incoming high-velocity particle. The getter can be mounted in air ducts to serve as a filter in operating rooms in hospitals, clean rooms and other areas where clean air is crucial.

Non inorganic aerogels have also been developed which are suitable as filtering media. Organic aerogel microspheres (diameters ranging from about 1 micron to about 3 mm), based on the resorcinol formaldehyde compound, can be formed by stirring the aqueous organic phase in mineral oil at elevated temperature. The dispersed organic phase polymerizes and forms non-sticky gel spheres. The size of the microspheres depends on the collision rate of the liquid droplets and the reaction rate of the monomers from which the aqueous solution is formed. The collision rate is governed by the volume ratio of the aqueous solution to the mineral oil and the shear rate, while the reaction rate is governed by the chemical formulation and the curing temperature. The microspheres can be pyrolyzed to form carbon aerogel microspheres [174]. Organic aerogel foams can be made from other precursors such as trimethylolpropane trimethacrylate and/or ethoxylated trimethylol trimethacrylate. These foams are ideally suited for filtering media, and especially for microorganism filtration for capture of bacteria, viruses, yeast and other microparticles [175].

15. Catalytic Filtration

Detoxification of air is very attractive for a whole host of applications not least for incoming air in a breathing mask. This approach should place less emphasis on the adsorptive capacity of the filter and may even require less material overall, depending on its effectiveness.

Aerogels containing silver nanoparticles have been made using a colloidal technique for gas catalysis [176]. The incorporation of silver at these small sizes,

in a high surface area and low resistance aerogel could offer interesting possibilities for chemical detoxification in a breathing device.

Catalytic aerogels, as mentioned previously, could potentially be very effective in terms of catalytic detoxification. Aerogels or xerogels containing atomically dispersed noble metals for applications such as environmental remediation have been made [137]. In order to bridge the incompatibility between noble metals and oxygen, new noble metal precursors, such as Pt-Si or Pd(Si-P)₂, were created and subsequently incorporated into the aerogel or xerogel by sol-gel processing. These were found to be effective for the oxidation of hydrocarbons, the reduction of nitrogen oxide species and the complete oxidation of volatile organic carbon species. Finely divided composite materials, reported in a patent [177], were made for the destructive adsorption of undesirable fluids in gaseous or liquid form, such as chlorocarbons and chlorofluorocarbons. These catalysts consisted of a first metal oxide (e.g., MgO) which was partially coated with an extremely thin layer of a second metal oxide, selected from the group of transition metal oxides such as Fe₂O₃. These composites were very effective for the destructive adsorption of the aforementioned compounds. Testing was carried out in a fluid stream containing the undesirable fluids, which contacted the composite, in the form of a filter. Other composites were made from particles of a first metal oxide selected from the group including MgO, CaO, Al₂O₃, SnO₂ and TiO₂, with the first metal oxide being at least partially coated with a second metal oxide different to the first, selected from the group comprising TiO₂, V₂O₅, Cr₂O₃, Mn₂O₃, Fe₂O₃, Cu₂O, CoO which could also include a mixture of these oxides. In an earlier patent [178], a catalyst for the destructive oxidation of toxic organic chemicals consisting of a metal or metal oxide impregnated on, or dispersed in an alkaline earth metal carbonate was described. The method provided for the destructive oxidation of hydrocarbon and halocarbons and their conversion into non-toxic by-products. The catalyst was composed essentially of a metal, selected from the group of manganese, copper, silver, iron, aluminum, or a metal oxide selected from the group consisting of nickel oxide, cobalt oxide, aluminum oxide, vanadium oxide, tungsten oxide, molybdenum oxide, or mixtures thereof. This was then impregnated onto, or dispersed in an alkali metal carbonate, alkali metal bicarbonate, alkaline earth metal carbonate, alkaline earth metal bicarbonate, or their mixtures.

Evidently the filtration field is an expanding one which is examining new and different adsorbents that can also act catalytically to decompose and so detoxify the air, gas stream or liquid media in which it is operating. Catalytic detoxification offers the possibility of reduced filter volume, while a combination of new and traditional materials acting as adsorbents and /or catalysts may well broaden the range of toxins which the filter can handle. Composite materials further extend these possibilities from purely chemical considerations through to the mechanical. The key may well lie in preparing a multicomponent layered filter

bed of several filtering components which may include composites (e.g. metal oxides in a carbon foam) to deal with several toxins either individually or collectively in the field. The possibility of monolithic filters, such as the composites developed in this laboratory [165], which could be cast to the shape of the container, would provide several such mechanical advantages. Activated carbon incorporated into a thermoset matrix, such as that derived from resorcinol formaldehyde, would be another example of such composite technology.

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17. Appendix - Literature Search

Several on-line searches were conducted for this report. The database files of the Dialog index, including chemical abstracts formed the exclusive source of many of the references. These files will be itemized below. Other sources included the author's own work experience, two authoritarian text books on the subject, books of collected papers, and the personal literature on the subject acquired by the author which include articles from journals, conference proceedings and the like.

A print out of the various files searched is given in table ALS accompanying this appendix.

A CD-ROM search of EI-Compendex for the last five years was conducted and several files in the Dialog dialindex which were defence oriented. The EI-compendex file was also searched in Dialog yielding several references. The defence oriented files however produced zero items. Most files were a collection of other databases and the defence files were no exception. The defence files were: DEFBUS (Defence and Aerospace Industry), DEFTAPS (Defence and Aerospace Industry on ONTAPS - Online Training), and DEFTECH (Defense Technology). These files only collected information relevant to certain defense interests and were not any kind of defense database as such.

A complete listing of all Dialog files in the master index and more information can be found at:

<http://library.dialog.com/bluesheets/html/bls.html>

As might be expected chemical abstracts contained th majority of the relevant articles but some useful references were found in other files, particularly for the search on aerogels and xerogels as filters.

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Your SELECT statement is: - s aerogel? and (filtration or filter?)

Items File

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4  2: INSPEC_1969-1999/JUN W3
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11 8: EI COMPENDEX(R)_1970-1999/JUN W3
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N18 0 99: Wilson Appl. Sci & Tech Abs_1983-1999/May
N19 0 238: Abs. in New Tech & Eng_1981-1999/Jun
N20 0 240: PAPERCHEM_1967-1999/May

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N21 0 335: Ceramic Abstracts_1976-1999/Q4
N22 0 434: SciSearch(R) Cited Ref Sci_1974-1989/Dec

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Table ALS-II. Dialog database search for aerogels/ xerogels and filtration.

Table 8. Survey of metal ions adsorbed on silica

Element	Reference	Remarks
Monovalent ions		
Thallium	Vydra and Markova [54]	Ethylenediamine complex (en)
Silver	Vydra and Markova [54] Smith and Jacobson [55]	Ethylenediamine complex (en) Ammine and en complexes
Divalent ions		
Calcium	Carroll and Freeman [56] Iler [56] Greenberg [57] Tadros and Lyklema [58] Wakatsuki, Furakawa and Kawaguchi [59] Dushina et al. [60]	Depends on particle size of SiO_2 Interaction with Li Adsorption data
Strontium, barium	Carroll and Freeman [56] Wakatsuki, Furakawa and Kawaguchi [59] Read and Kitchener [61]	
Magnesium	Dushina et al. [60]	Adsorption data
Manganese	Taniguchi et al. [62]	Coord. by 1 SiO^- ion
Nickel	Vydra and Markova [51] Smith and Jacobson [55] Taniguchi et al. [62] Dushina et al. [63] Kaverinski et al. [64]	Ethylenediamine complex (en) Ammine and en complexes Coord. by 2 SiO^- ions Ammine complexes Ni can coord. With polar ligands
Cobalt	Healy, James and Cooper [65] Wakatsuki, Furakawa and Kawaguchi [59] Burwell et al. [66] Vydra and Markova [51] Smith and Jacobson [55] Taniguchi et al. [62] Brotikovskii et al. [67] James, Wiese and Healy [68]	Chloro and en complexes Ethylenediamine complex (en) Ammine and en complexes Coord. by 1 SiO^- ion State of Co on surface
Copper	Schindler et al. [69] Kolthoff and Stenger [54] Vydra and Markova [54] Hathaway and Lewis [70] Smith and Jacobson [55] Taniguchi et al. [62] Dushina et al. [60]	Ethylenediamine complex (en) Several ligands Ammine and en complexes Coord. by 1 SiO^- ion Adsorption data

Zinc	Wakatsuki, Furakawa and Kawaguchi [59] Kozawa [71] Vydra and Markova [54] Smith and Jacobson [55] Taniguchi et al. [62] Dushina et al. [60]	Ethylenediamine complex (en) Ammine and en complexes Coord. by 2 SiO ⁻ ions Adsorption data
Chromium (II)	Hierl and Krauss [72]	Cr ²⁺ -NH ₃ complexes stabilized
Cadmium	Schindler et al. [69] Kalatsei et al. [73] Dushina et al. [60]	Cd attacks surface in NH ₃ solu Adsorption data
Tin (II)	Suzdalev et al. [74] Goldanskii et al. [75]	Using Mossbauer effect Using Mossbauer effect
Lead	Schindler et al. [69] Thompson [76]	Pb removed from molten Bi
Palladium	Sulcek, Vasak and Dolezal [77] Dushina et al. [60]	Adsorption data
Trivalent ions		
Yttrium	Wakatsuki, Furakawa and Kawaguchi [59]	
Lanthanum	Read and Kitchener [61] James, Wiese and Healy [68]	
Gallium	Wakatsuki, Furakawa and Kawaguchi [59]	
Aluminum	Stanton et al. [78] French and Howard [79] Arhland et al. [49] Kohlschutter et al. [80] Matijevic et al. [81] Wakatsuki, Furakawa and Kawaguchi [59] Matijevic [82] Vydra and Calba [83]	
Chromium (III)	Arhland et al. [49] Stanton and Maatman [50] Wakatsuki, Furakawa and Kawaguchi [59] Healy, James and Cooper [65] Cornett and Burwell [84] Vydra and Calba [83]	(CrCl ₂ ·4H ₂ O) ⁺ is adsorbed not Cr ³⁺ Adsorbed >pH 4 as neutral hydroxide

Iron (III)	Arhland et al. [49] Stanton and Maatman [50] Stanton et al. [78] French and Howard [79] Pott and McNicol [85] Schenk and Weber [86] Schindler [69] Healy, Cooper and James [87] Vydra and Calba [83]	Adsorption depends on anions
Antimony	Eschrich et al. [8]	Adsorbed from strong acid
Tetravalent ions		
Zirconium	Akatsu et al. [89] Caletka [90] Caletka [91] Caletka [92] Caletka and Kyr [93]	Adsorbed from acid solution Separation from Hf Adsorbed only as hydrolyzed species Adsorption on hydrophobic SiO_2 ZrO_2 colloid adsorbed; Zr^{4+} in 2M HNO_3
Hafnium	Caletka [92] Caletka [91] Caletka [90]	Adsorption on hydrophobic SiO_2 Adsorbed only as hydrolyzed species Separation from Zr
Tantalum	Caletka and Kyr [93]	Adsorbed even from 10M acids
Niobium	Caletka [94] Akatsu et al. [89]	Adsorbed as neutral complexes Adsorbed from up to 6M acids Adsorbed from acid solution
Thorium	Vydra and Calba [83] French and Howard [79] Kohlschuetter and Katzenmeyer [95] James, Wiese and Healy [68]	Adsorbed above pH 1.5 Probably adsorbed as polycations
Protactinium	Caletka [96]	Adsorbed strongly and separated from Th, U, Zr, Hf, Nb
Plutonium	Davydov [97] Stanton et al. [78] French and Howard [79] Rozell and Andelman [98] Grebenshchikova [99]	$\text{Pu}(\text{OH})_n^{64-80+}$ adsorbed above pH 1 Adsorbed from 10^{-7} sol, neutral pH Adsorbed at pH 0.6-4.5
Hexavalent ions		
Chromium (VI) Dichromate	Pukkukat [100] Maatman [101]	Cr^{6+} stabilized to 565°C, polym. Cat. $\text{SiOCr}(\text{O})_2\text{OCr}(\text{O})_2\text{OH}$
Uranium (VI)	Zakı and Abd-EL-Moneim [102] Stanton and Maatman [49] Arhland [49]	Adsorbed on SiO_2 at var. Temps.

Stanton et al. [78]
French and Howard [79]
Kobyshev [103]



Figure 1. Aerogel monolith. This low density structure slows sound waves, is the most insulating material known and has the lowest refractive index next to air.